Protecting Wild Rice From Excess Sulfate: Proposed Approach

May 19, 2015

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CLEAN WATER LAND & LEGACY AMENDMENT

Minnesota Pollution Control Agency

Objectives for Today

- Welcome/Introductions/Overview
- Presentation of the Proposed Approach
- Group Discussion, including input on:
  - Additional information to inform the proposed approach
  - Outstanding implementation questions
- Next Steps
  - Data collection and analysis
  - Feedback/input
  - Advisory Committee meetings

CLEAN WATER LAND & LEGACY AMENDMENT

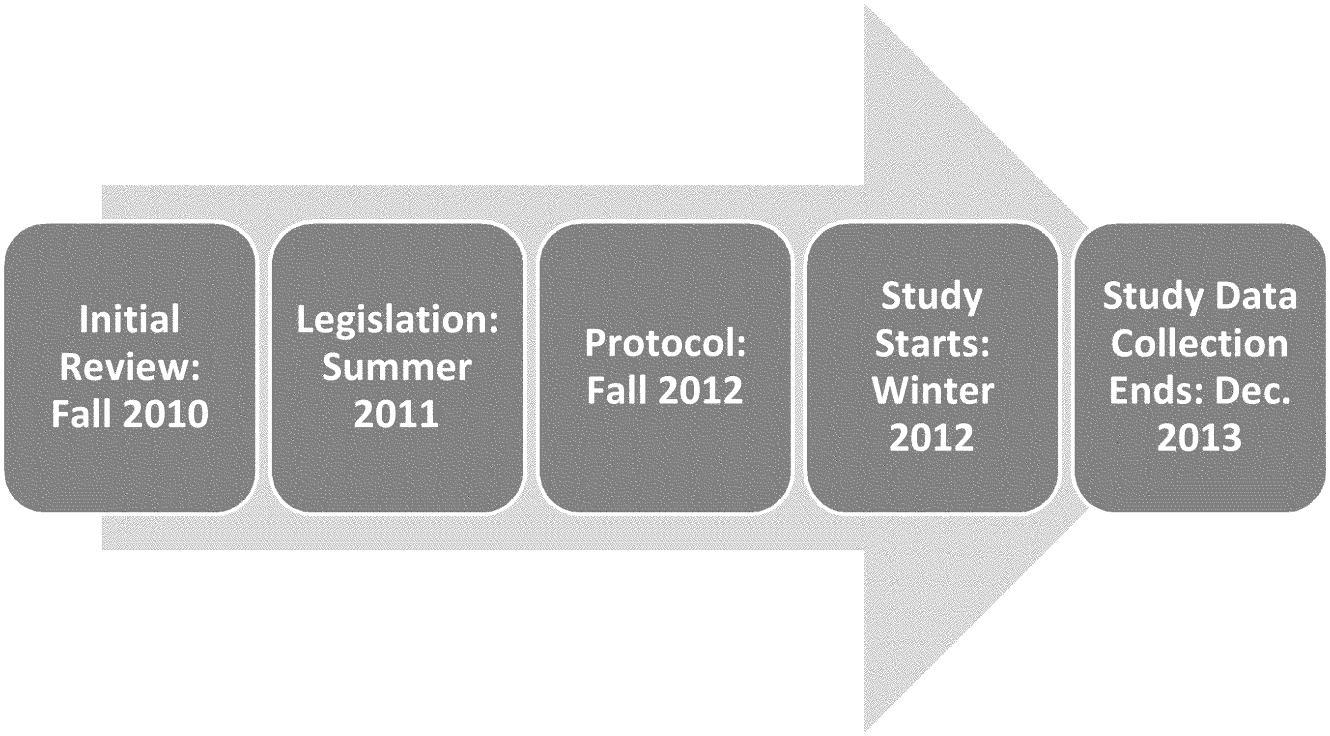
Who Are We?

- Purpose (Laws of MN 2011, 1st Spec. Sess., Ch. 2, Art. 4, Sect. 32(c)):
  1. Provide input to the commissioner on a protocol for scientific research to assess the impacts of sulfates and other substances on the growth of wild rice,
  2. Review research results, and
  3. Provide other advice on the development of future rule amendments to protect wild rice.
- Include representatives of tribal governments, municipal wastewater treatment facilities, industrial dischargers, wild rice harvesters, wild rice research experts, and citizen organizations.

Principles and Goals

- Input from varied interests and expertise
- Transparency
- Inclusive approach
- Common understanding of the study purpose and progress
- Learn from related research efforts

Where Have We Been?

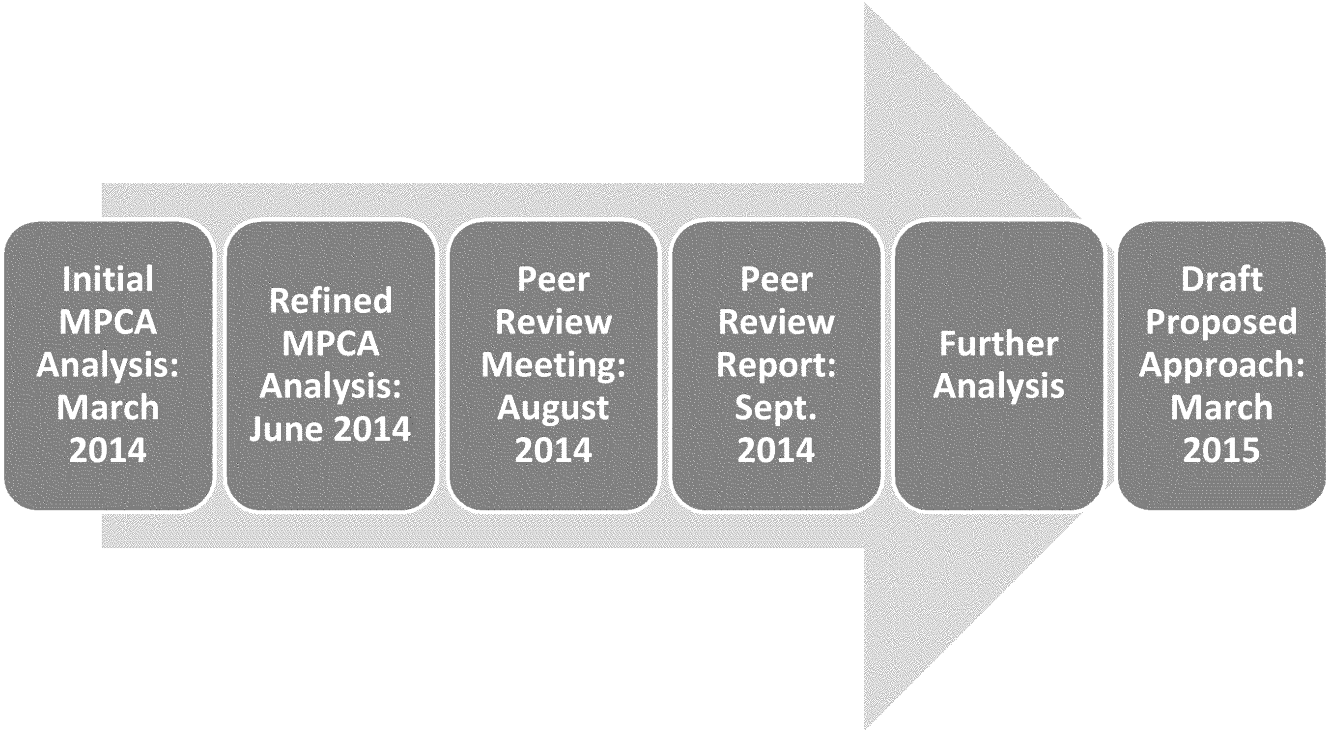


Wild Rice Standard Study

- Goal: Enhance understanding of the effects of sulfate on wild rice; inform standard evaluation
- Key avenues of investigation:
  - Laboratory experiments
  - Mesocosm experiments
  - Field survey
  - Sediment experiments

- Any standard modification will be based on multiple information sources

Where Have We Been, Cont.?



Draft Proposal for Protecting Wild Rice from Excess Sulfate: March 2015

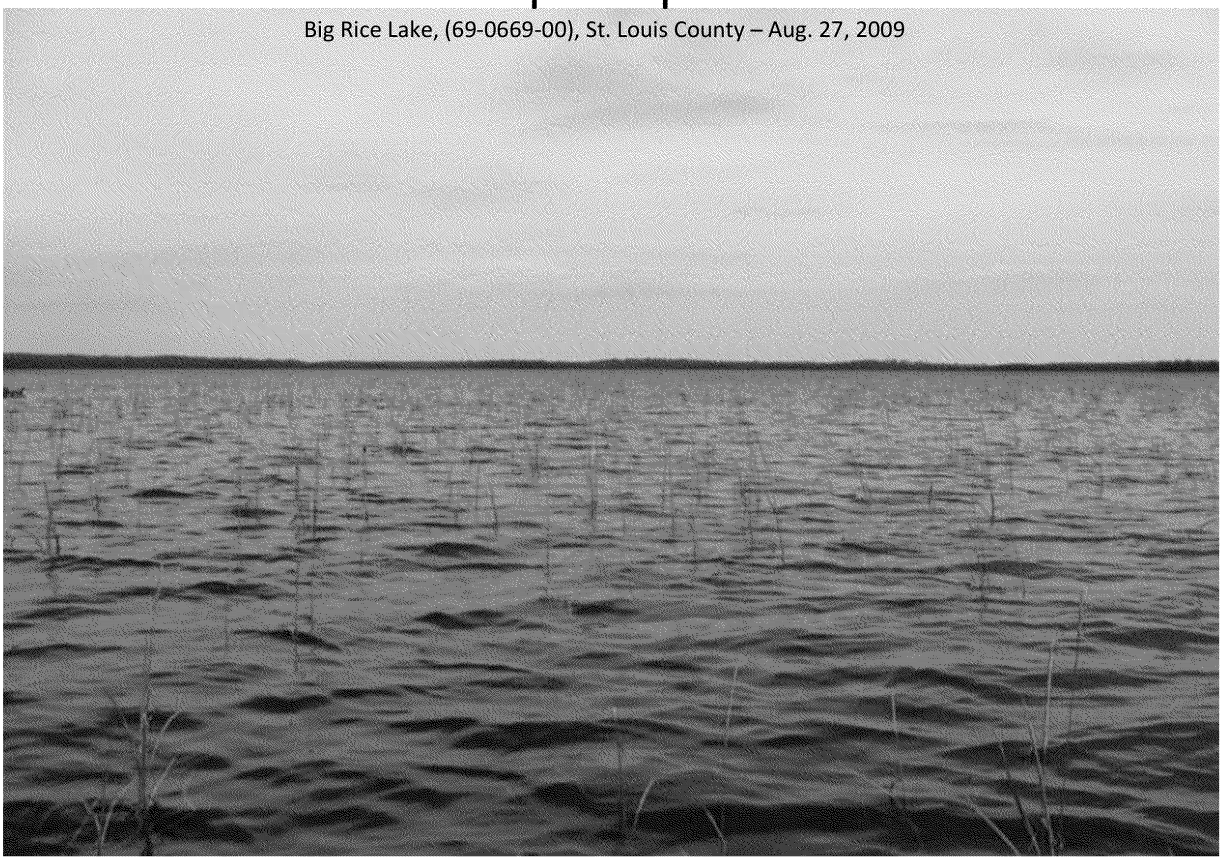
- Draft definition and list of “wild rice waters”
- Proposed approach to “the standard”
- Implementation questions

Draft wild rice waters list and definition

A surface water of the state that contains a self-perpetuating population of wild rice plants, either currently present or that have been present in the given water body since November 28, 1975. The self-perpetuating wild rice population must be represented by a minimum of 8,000 wild rice stems over the surface of a lake, wetland, or reservoir water body or a minimum of 800 wild rice stems over a river-mile reach for a riverine water body. Waters designated as wild rice waters are specifically listed as such in Minn. R. 7050.0470 and are identified with the symbol [WR] preceding the name of the water body.

Visual representation of a lake with approx. two wild rice stems per square meter

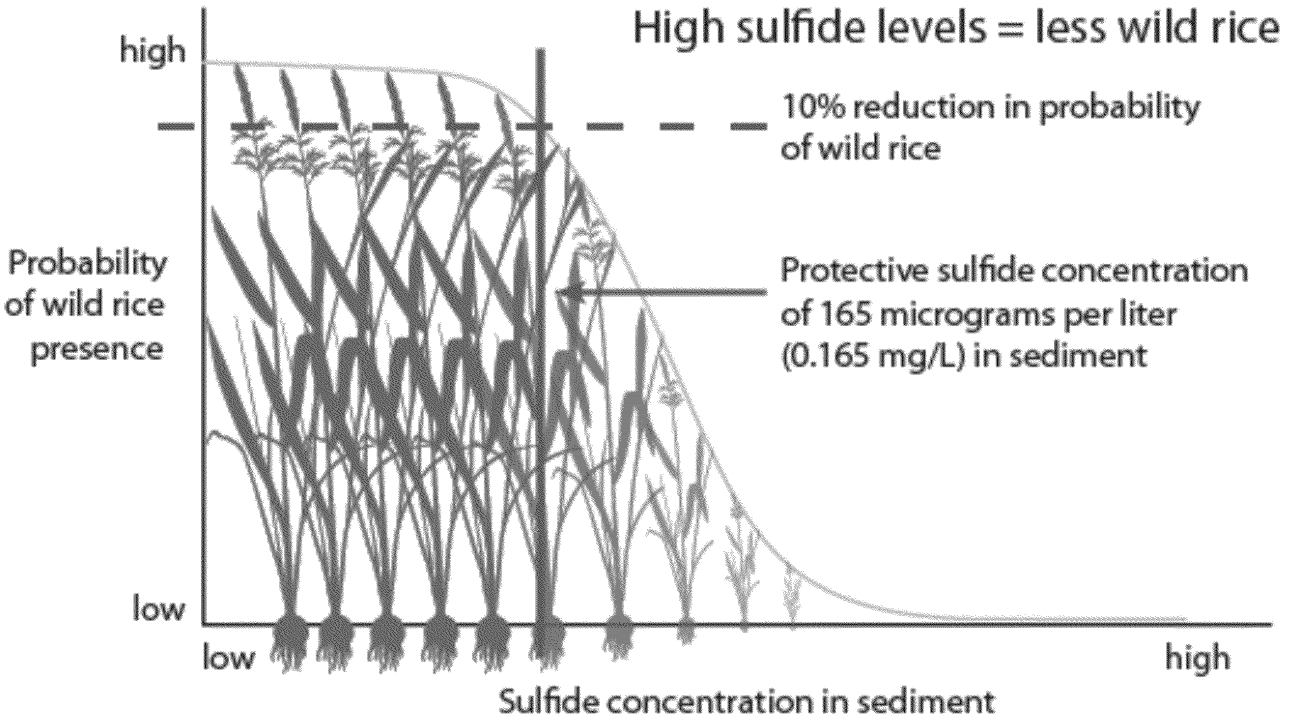
Big Rice Lake, (69-0669-00), St. Louis County – Aug. 27, 2009



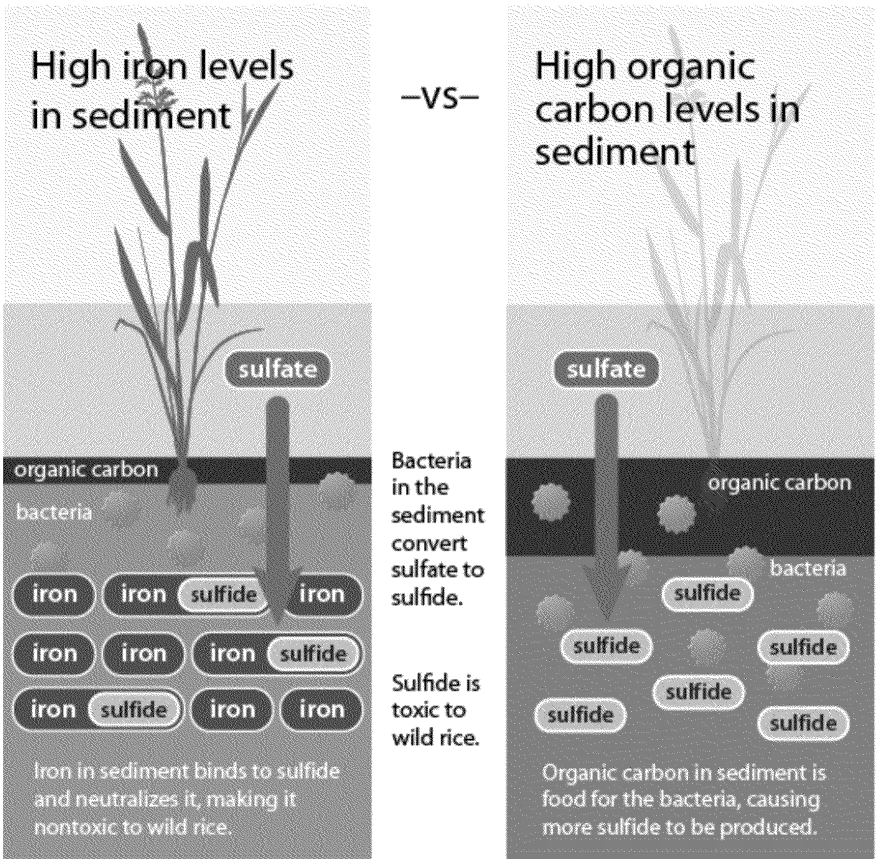
Draft wild rice waters – sources of information considered

- DNR 2008 Wild Rice Report, Appendix B inventory lists 1286 water bodies, approximately 60% have estimated acreages. Waters with acreage estimates > 2 acres are included
- DNR 2007 Wild Rice Harvester Survey
- DNR 2010 Minnesota Interagency Wild Rice Management Workgroup List, contains 350 significant wild rice resources, most of which were listed in the MDNR 2008 report
- DNR's 2011 County Biological Survey, waterbodies with descriptors such as "thick wild rice present" or "emergent aquatic plant community dominated by wild rice" are included
- DNR Responses to MPCA 2013 "Call for Data", waters that have estimated wild rice acreage of > 2 acres are included
- DNR Aquatic Plant Management database, contains multi-year wild rice permit information for the removal of wild rice or restoration permits for seeding wild rice
- MPCA Biomonitoring field database, queried for wild rice records from 1999 to 2014.
- 1854 Treaty Authority wild rice surveys
- Minn. R. 7050.0470, "WR" waters specifically listed in the rule in the Lake Superior watershed
- U o fM/MPCA field surveys from 2011, 2012, and 2013
- NPDES Permittee field surveys

Highlights of Proposed Approach: Sulfide



Sulfide – Sulfate Relationship



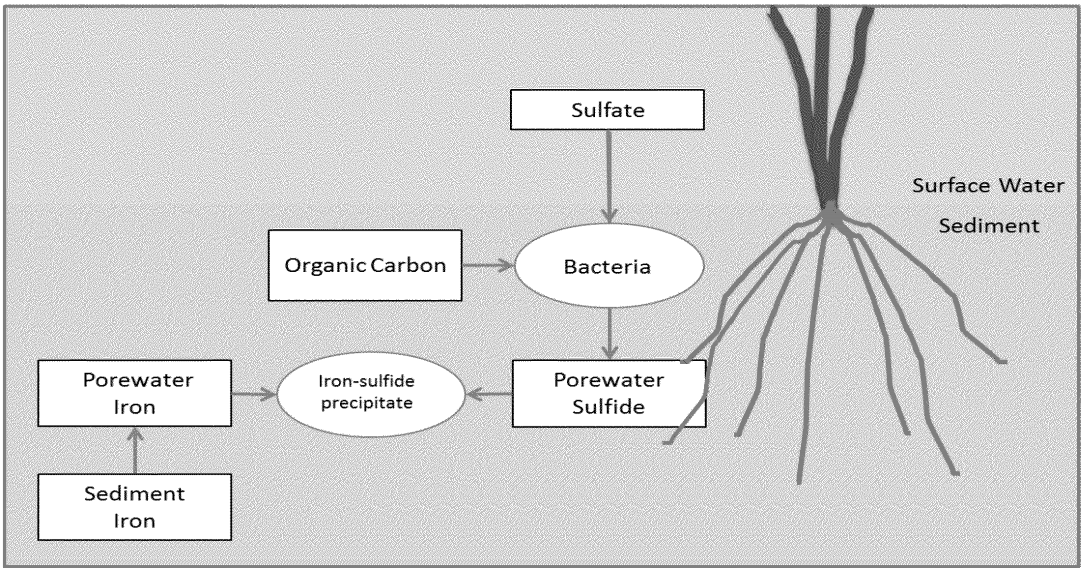
Proposed Equation to Protect Wild Rice: DRAFT

- Developed SEM relating sulfate, sulfide, iron and organic carbon
  - Multiple variables reviewed
  - Multiple regression also evaluated
  - SEM approach was more precise
- Integrated protective sulfide concentration (165 µg/L) into the modeled equation
- Evaluated strength of equation using boot-strapping and jack-knifing techniques

The Path From “Draft Analysis” to “Draft Proposed Approach”

Draft MPCA Analysis of the Study Data (June 2014)

- Conceptual model: sulfate, sulfide, and iron
- Analyzed field data with quantile regression
- Based on hydroponic results, likely protective concentration of sulfide was suggested to be 150 to 300 µg/L sulfide



Peer Review Panel

(Met August 2014; 9/25/2014 final report is on MPCA website)

- Dr. Patrick Brezonik (discussion chair), University of Minnesota (retired)
- Dr. Gertie Arts Wageningen University and Research Centre, Netherlands
- Dr. Donald Axelrad Florida A&M University
- Dr. Siobhan Fennessy Kenyon College
- Dr. Susan Galatowitsch University of Minnesota
- Dr. Mark Hanson University of Manitoba
- Dr. Curtis Pollman Aqua Lux Lucis, Inc.

Scientific Peer Review: Specific Conclusions

Hydroponic Experiments (p. 4)

- Demonstrated sulfide is the toxic agent to wild rice.
- Use of EC_{20} is not considered protective of wild rice.
- Use time-weighted sulfide concentrations instead of initial.
- Recommendation: Use logistic regression estimate of EC_5 or EC_{10} as protective concentration.
- Had recommendations if the experiments were to be repeated.

Scientific Peer Review: Specific Conclusions (continued)

Mesocosm Experiments (pp. 5-6)

- Served to characterize effects over full life cycle of wild rice.
- Recommendations:
  - Analyze plant responses relative to actual sulfate and sulfide exposure rather than nominal.
  - Use the mesocosm data to develop a population model to understand factors influencing population persistence.

Scientific Peer Review: Specific Conclusions (continued)

Field Survey (pp. 6-7)

- Provides a rich data set that can be used to describe effects of sulfide.
- Provides a means to determine a sulfide level protective of wild rice.
- Recommendations:
  - Perform additional statistical analyses to determine thresholds, or probability of wild rice occurrence, for sulfide, sulfate, and other parameters.
  - Further analysis of the existing data, with a more expanded set of variables.
  - Expand the complexity of the models to elucidate the interactions of the environmental variables.
  - Analyze data with stems per m^2 rather than percent wild rice cover. Consider quantifying number of flowering stems.

Scientific Peer Review: Overall Conclusions

- The study structure was appropriate to investigate effects of elevated sulfate. (p. 4)
- Taken together, the three study components provide support for the sulfate, sulfide, and iron paradigm. (p. 4)
- Sulfide levels above 300 µg/L can be toxic to wild rice, a conclusion supported by field survey and mesocosm data. (p. 7).
- Establishing a threshold for the onset of effects at or above 300 µg/L would likely result in ecologically significant adverse effects to wild rice. (p. 7)
- Consider use of SEM to model the relationship between sulfate and sulfide, while accounting for organic carbon and iron. (p. 8)
- Additional controlled lab studies targeted at how sulfide affects wild rice physiology and how that affects wild rice at the population level would be useful additions to the Study. (p. 4)

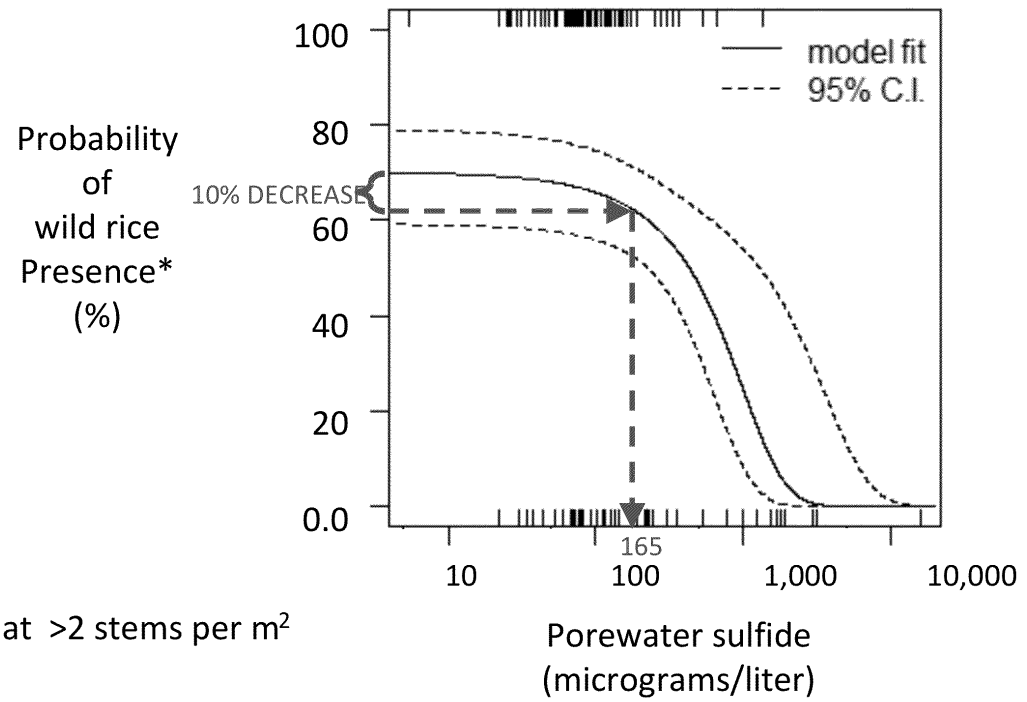
Further MPCA data analyses performed in response to the peer review

- Hydroponic data:
  - Merged three tests together for more statistical power; EC_{10} endpoint.
  - Analyzed time-weighted sulfide concentrations in addition to initial.
- Mesocosm data:
  - Analyzed dose-response relationships using measured sulfide concentrations.
  - In progress: effect of elevated sulfide on population dynamics of wild rice.
- Field survey data:
  - Examined effect of sulfide & other parameters on probability of wild rice occurrence (stems per m^2 rather than percent wild rice cover).
  - Examined variables that affect conversion of sulfate to sulfide with structural equation modeling (SEM) and multiple linear regression

March 2015 "*Proposed Approach*"

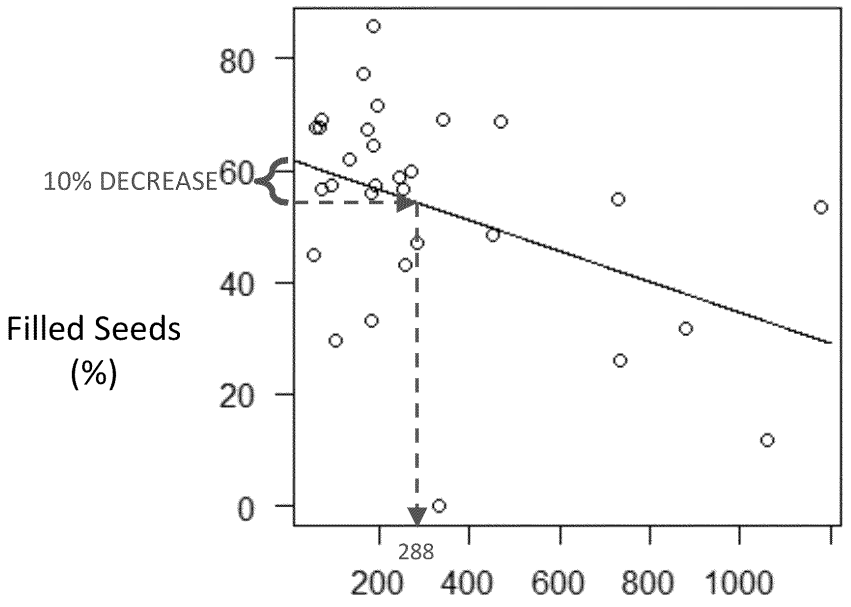
- Summary of study analyses
- Outline of proposed approach for protecting wild rice
- Considers questions of implementation

Binary logistic regression of wild rice presence against porewater sulfide: EC_{10} of 165 µg/L



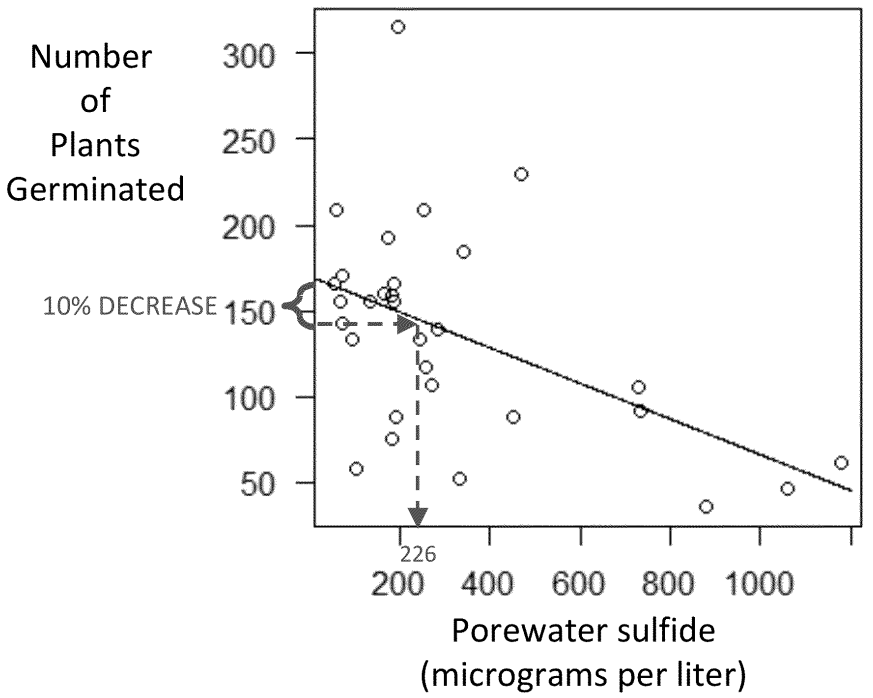
*Present at >2 stems per m^2

2013 Mesocosm Results: Relationship between porewater sulfide and percent filled seeds ($p < 0.02$)



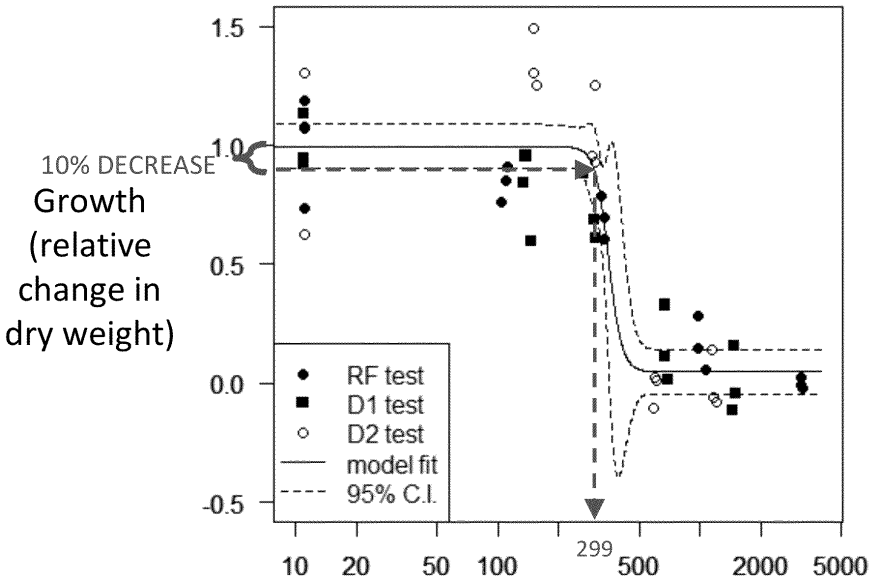
EC_{10} Values (µg/L)
143 (Log_{10} sulfide)
288 (linear sulfide)

2013 Mesocosm Results: Relationship between porewater sulfide and number of plants germinated ($p < 0.005$)



EC_{10} Values (µg/L)
121 (Log_{10} sulfide)
226 (linear sulfide)

Hydroponic exposure of wild rice seedlings to sulfide: Estimates of EC_{10} for 3 different assumptions of sulfide exposure



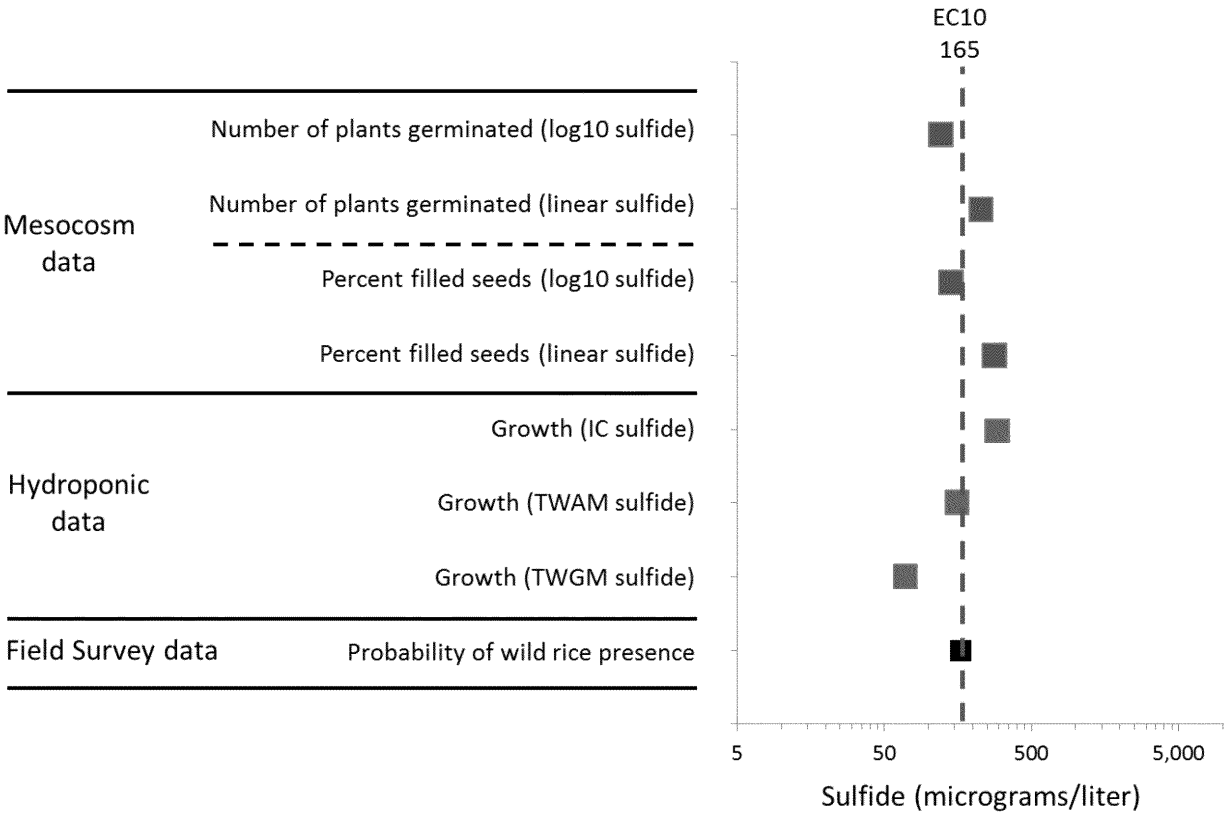
EC_{10} Values (µg/L)

299 (mean initial concentration)

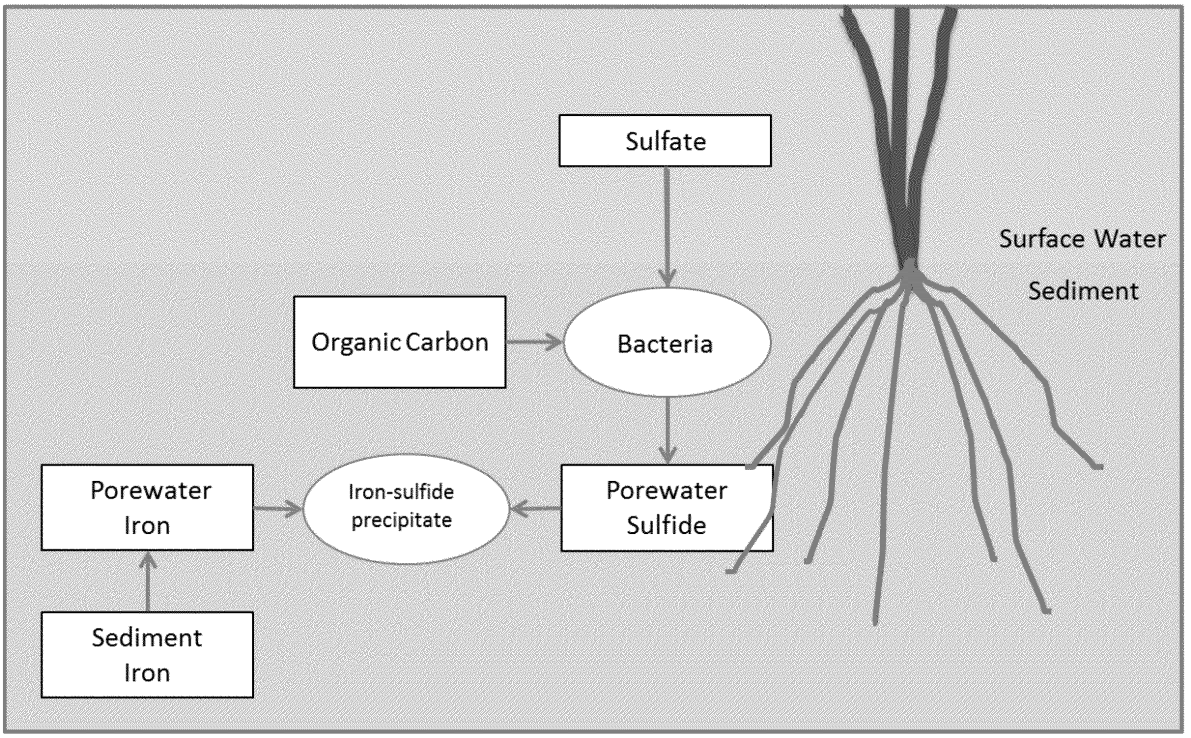
160 (time-weighted arithmetic mean)

71 (time-weighted geometric mean)

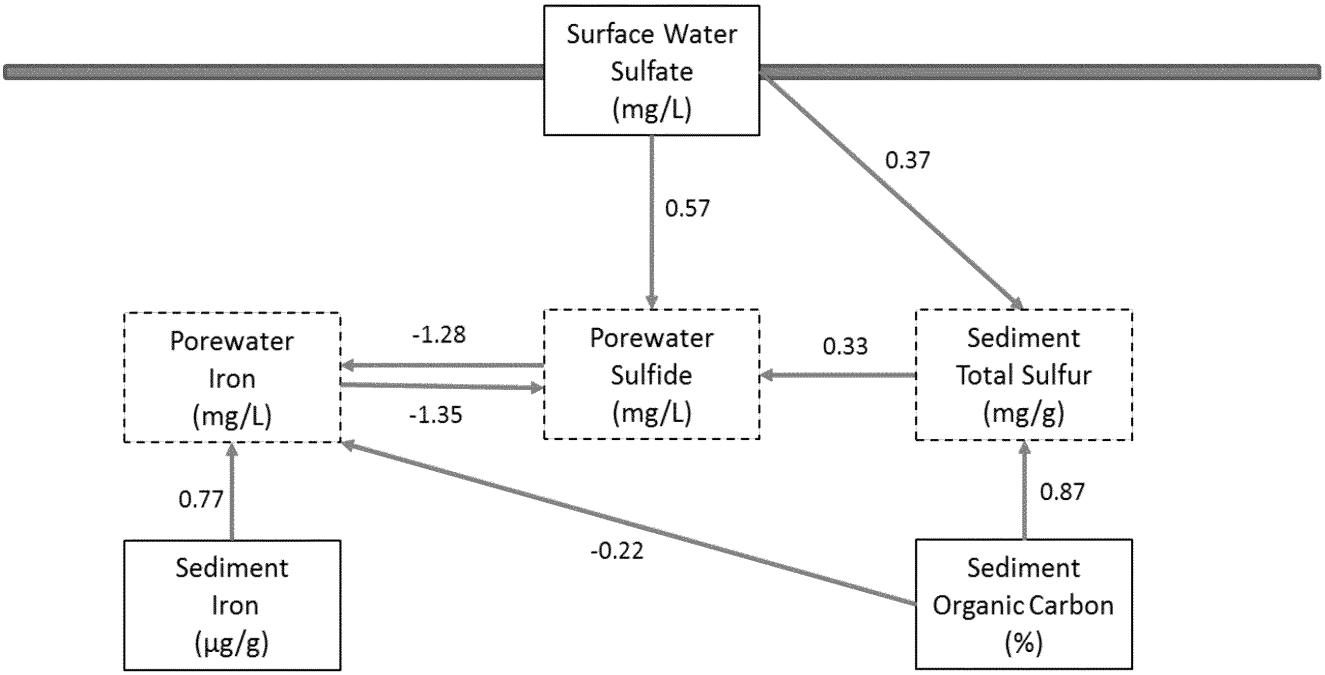
Comparison of EC_{10} values from the field survey to EC_{10} values produced by other study components.



Simplified diagram of the ways sulfate, sulfide, iron, and organic carbon interact

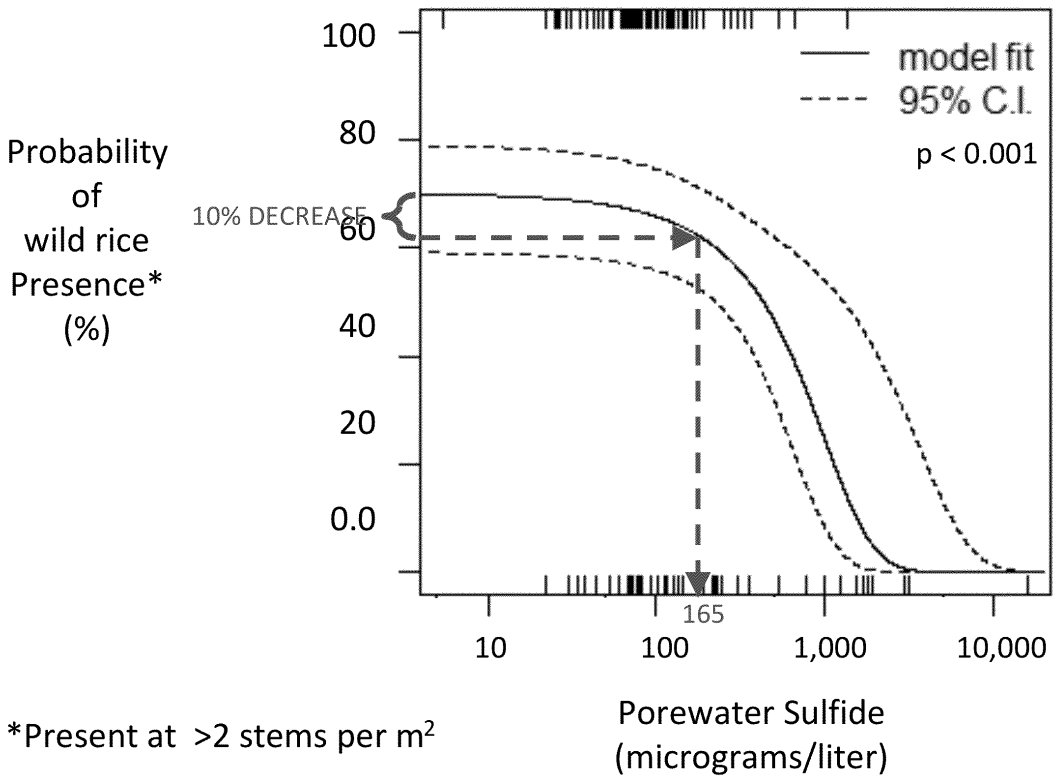


Structural equation model (SEM) of variables that control conversion of sulfate to sulfide



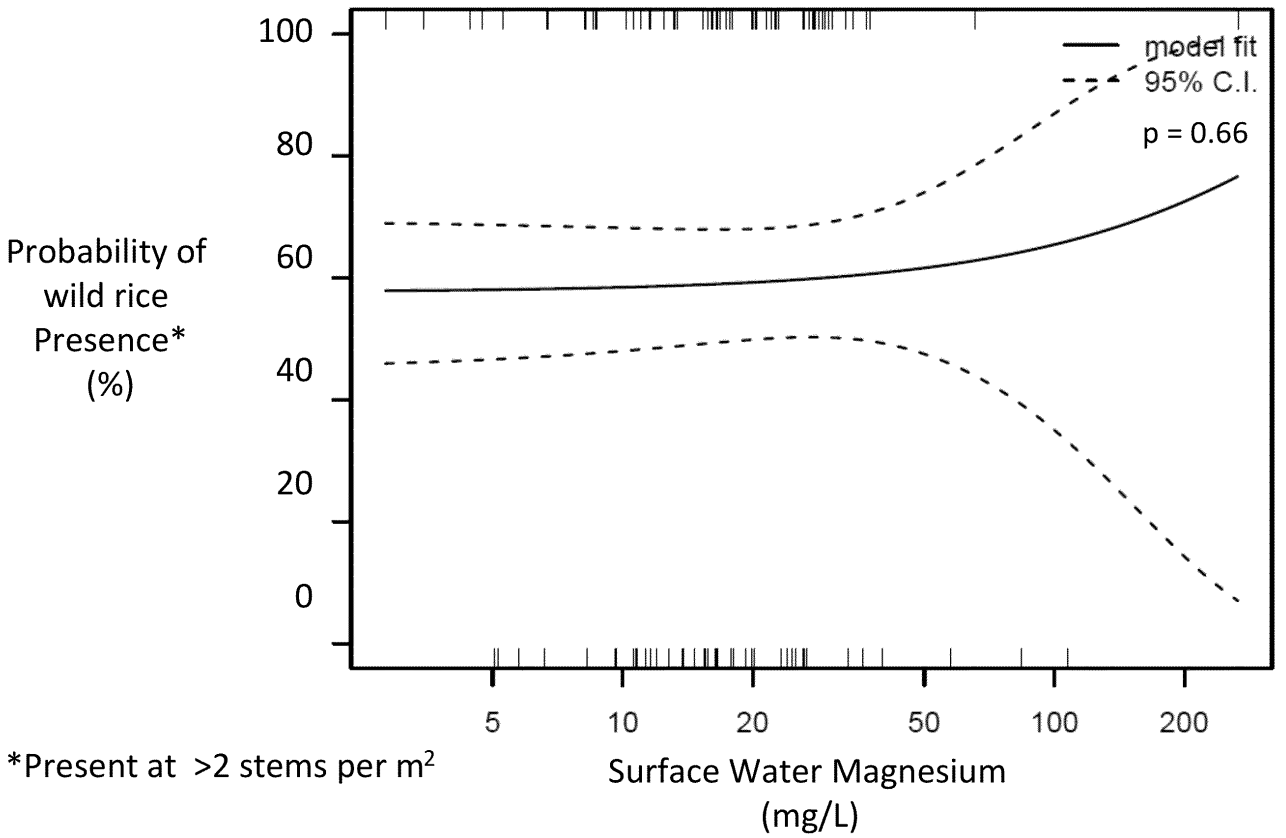
□ □ □ □ = 7.873 □□□□□□□□□□ 0.345 □ □ □ □ 0.486 □□□□□□□□□□ −0.675 □□□□□□□□□□

Binary logistic regression of wild rice presence against porewater sulfide: EC_{10} of 165 µg/L



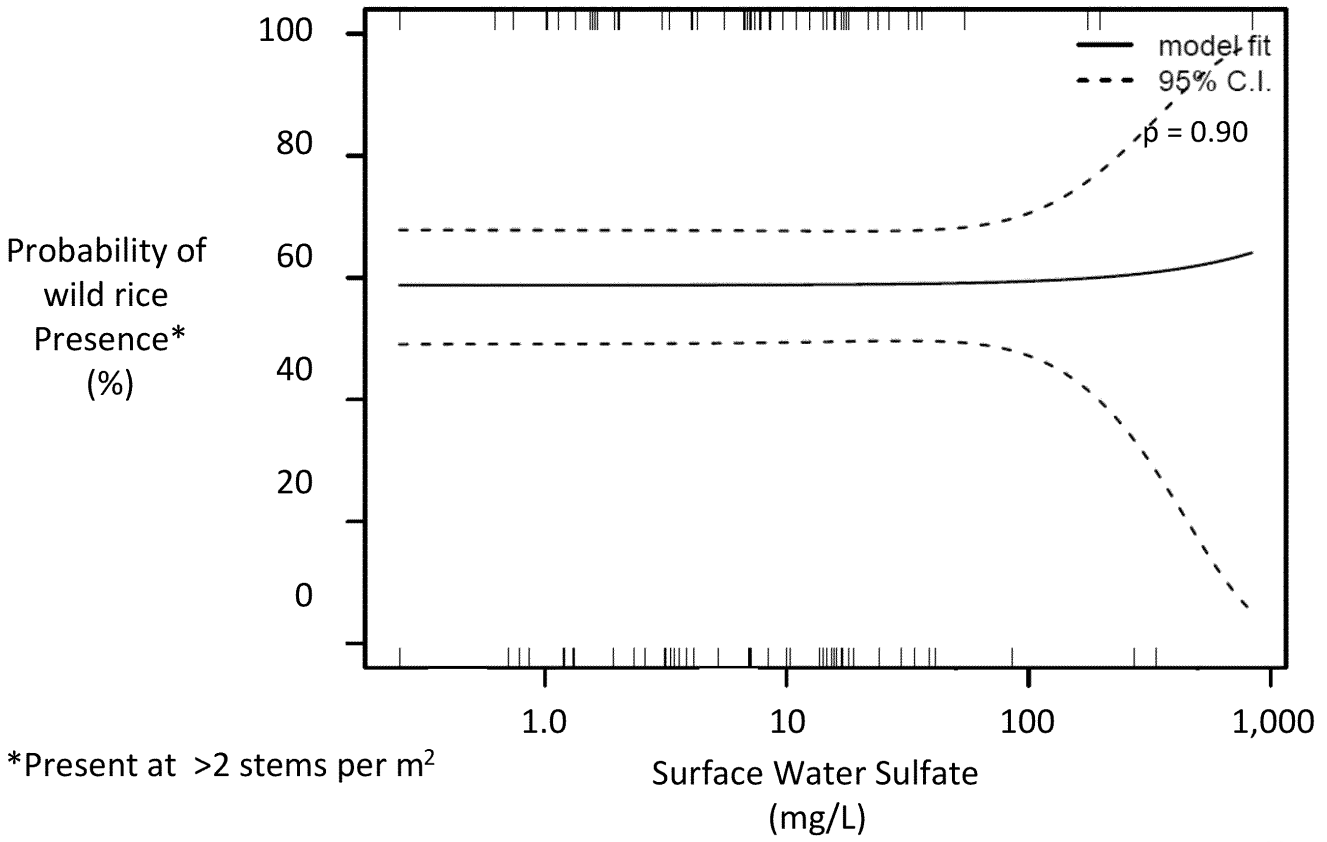
*Present at >2 stems per m^2

Probability of wild rice presence as a function of surface water magnesium



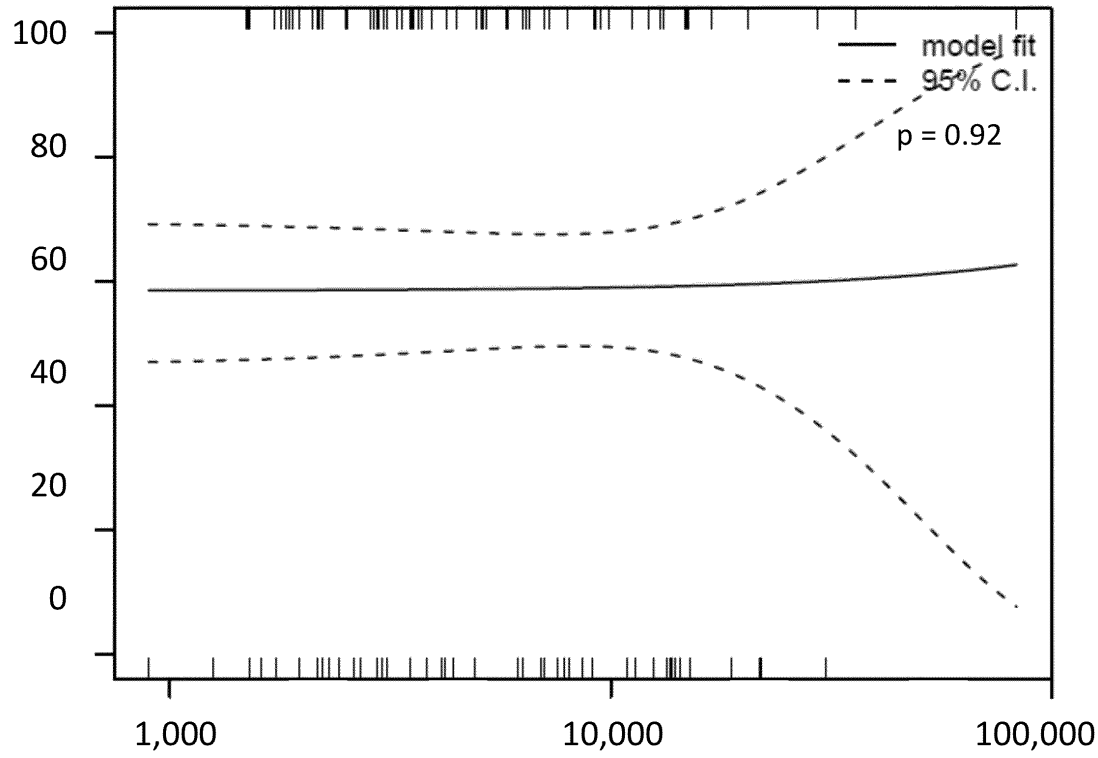
*Present at >2 stems per m^2

Probability of wild rice presence as a function of surface water sulfate



*Present at >2 stems per m^2

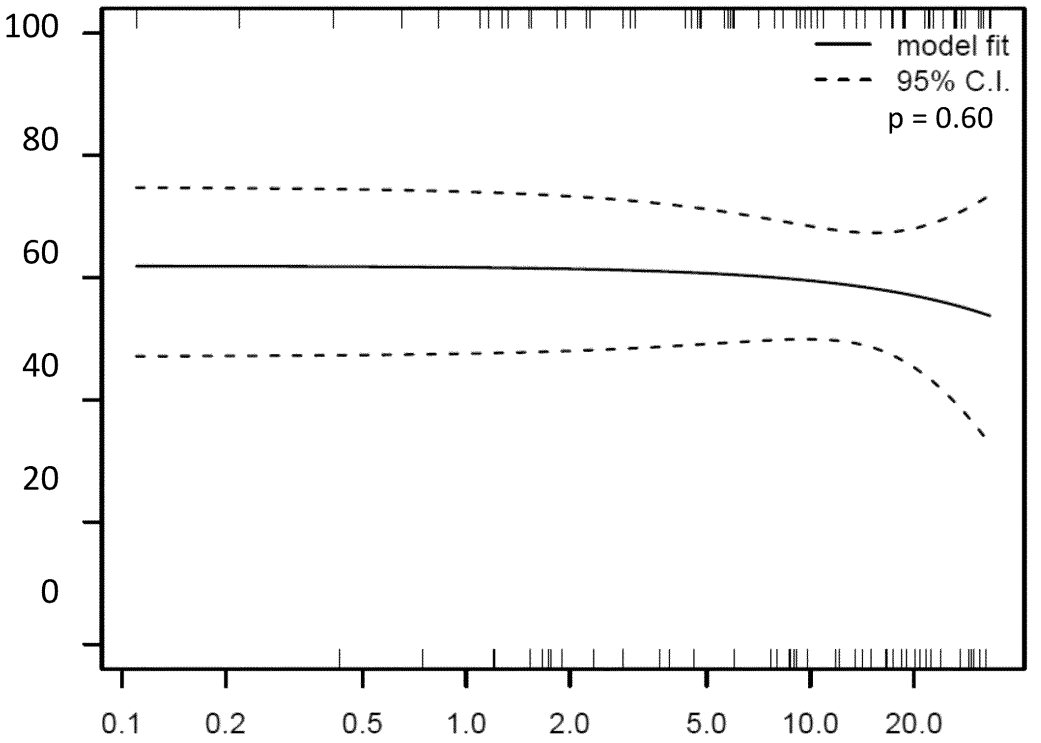
Probability of wild rice presence as a function of sediment iron



Probability of wild rice Presence* (%)

*Present at >2 stems per m^2

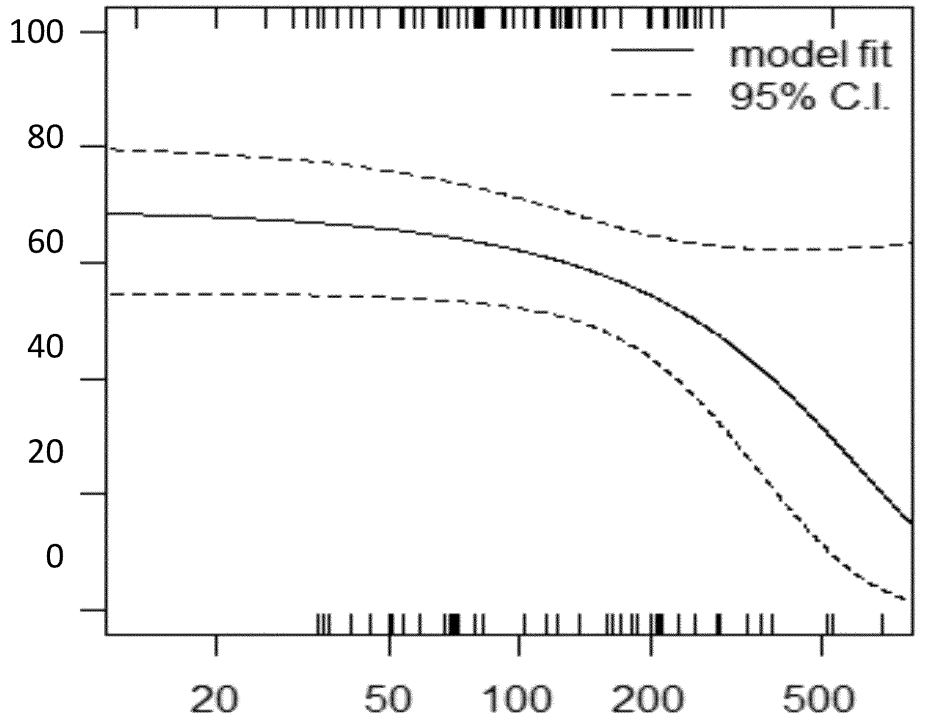
Probability of wild rice presence as a function of sediment total organic carbon



Probability of wild rice Presence* (%)

*Present at >2 stems per m^2

Probability of wild rice presence as a function of model-predicted porewater sulfide (based on sulfate, sediment iron, & sediment TOC)

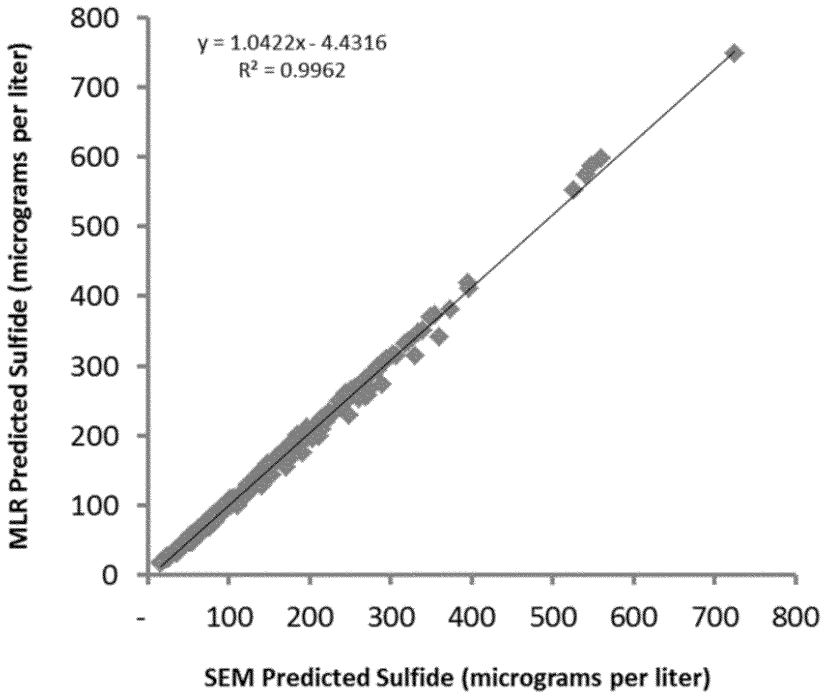


Probability of wild rice Presence* (%)

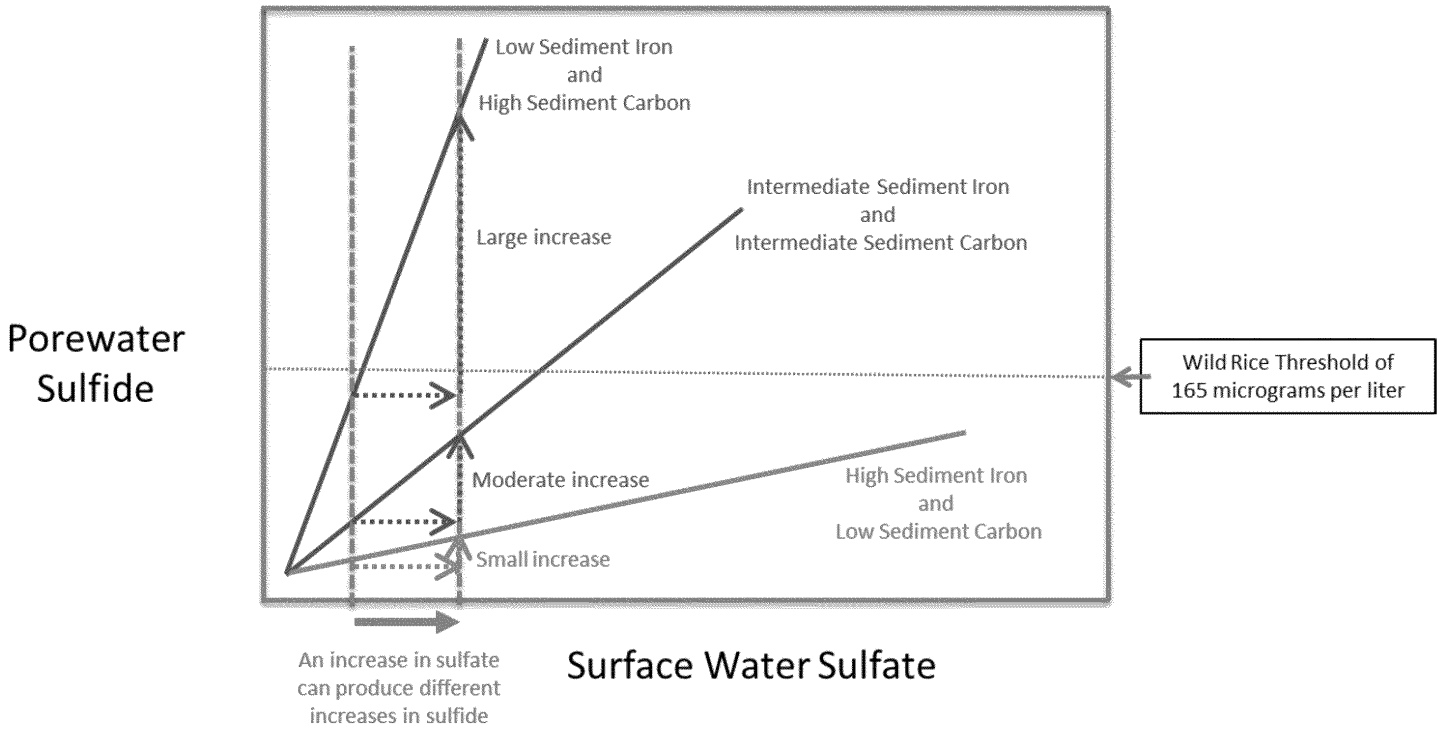
Modeled Porewater Sulfide (micrograms per liter)

*Present at >2 stems per m^2

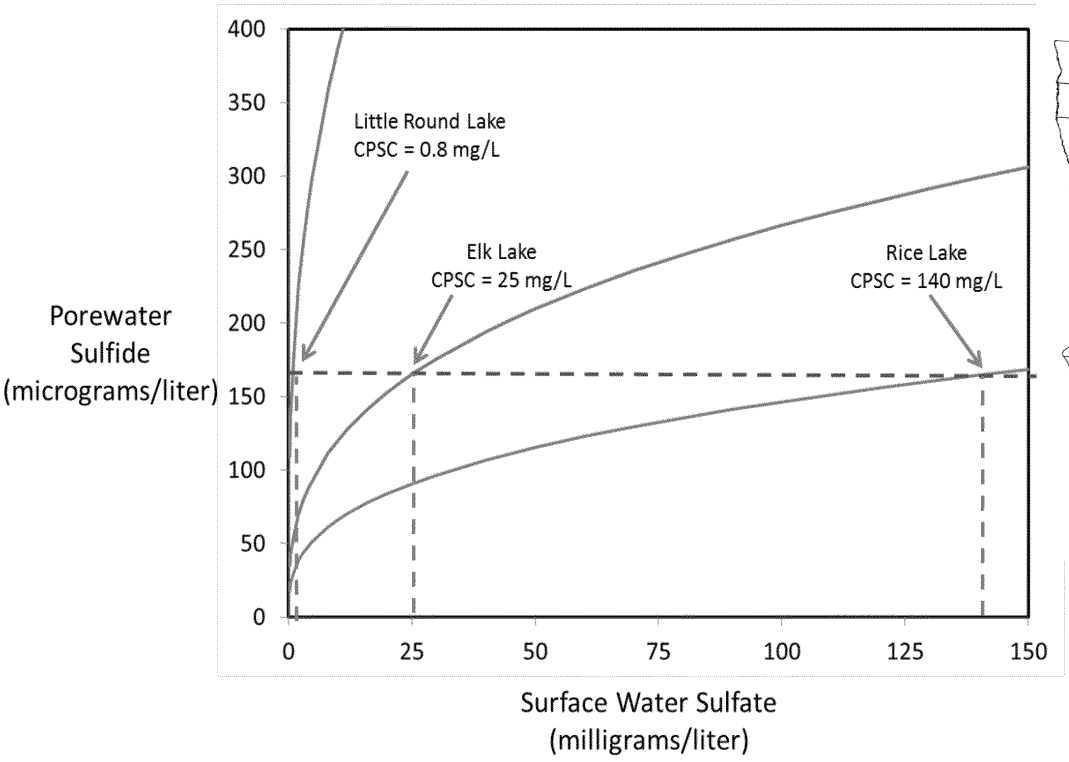
Comparison between porewater sulfide predicted by the structural equation model (SEM) and the multiple linear regression model (MLR)

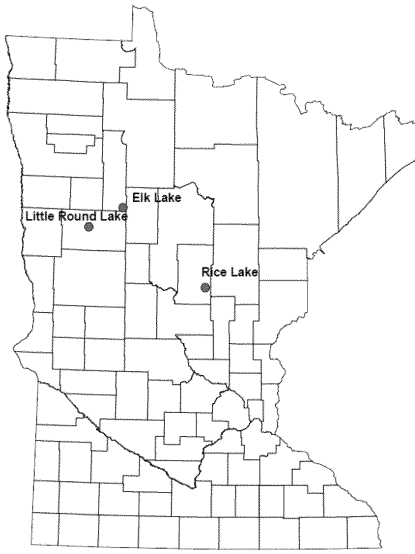


Qualitative SEM predicted relationships between sulfate in surface water & sulfide in porewater, as a function of sediment iron and organic carbon



Three wild rice lakes of contrasting sensitivity to sulfate (all have observed surface water sulfate < 0.5 mg/L)





Note: CPSC = Calculated Protective Sulfate Concentration

To calculate a protective sulfate concentration

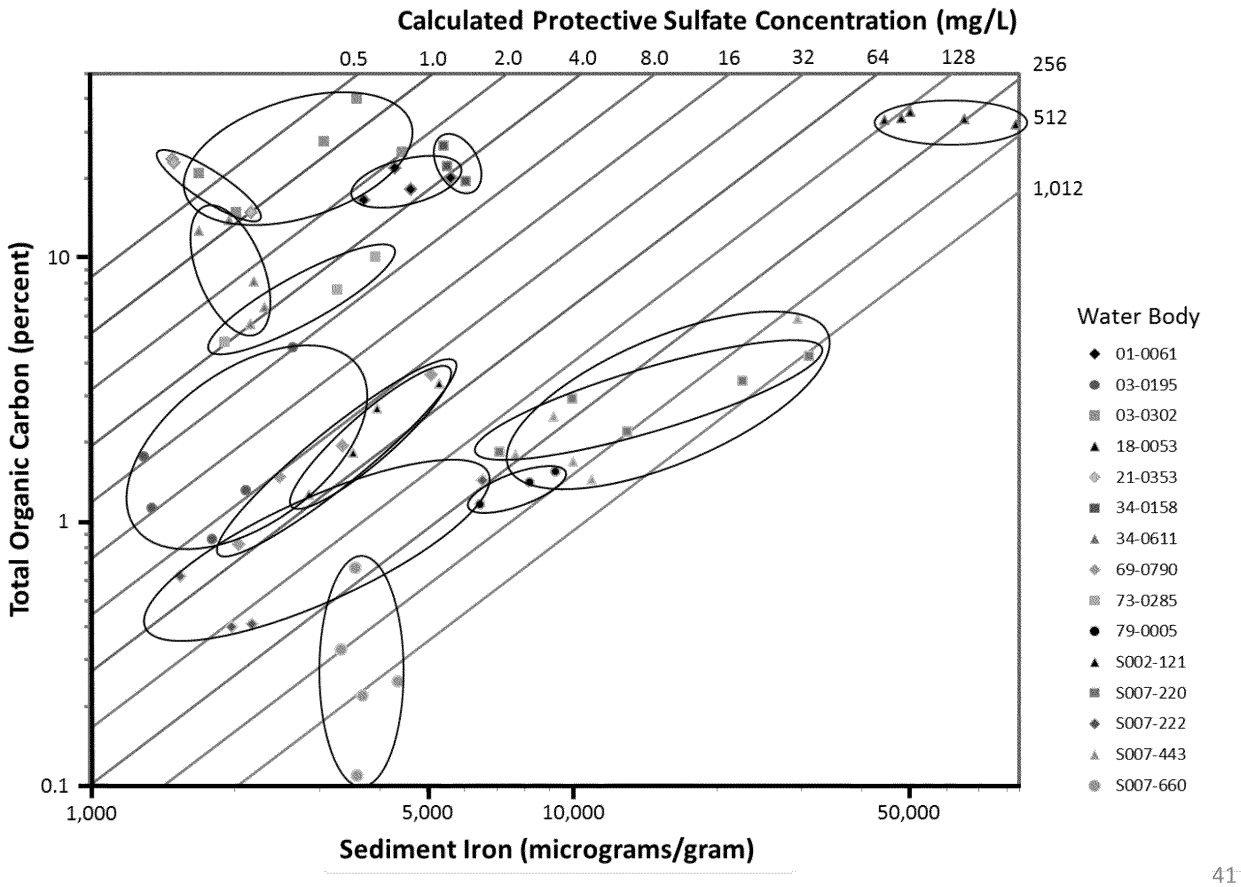
First, rearrange the SEM equation to solve for sulfate:

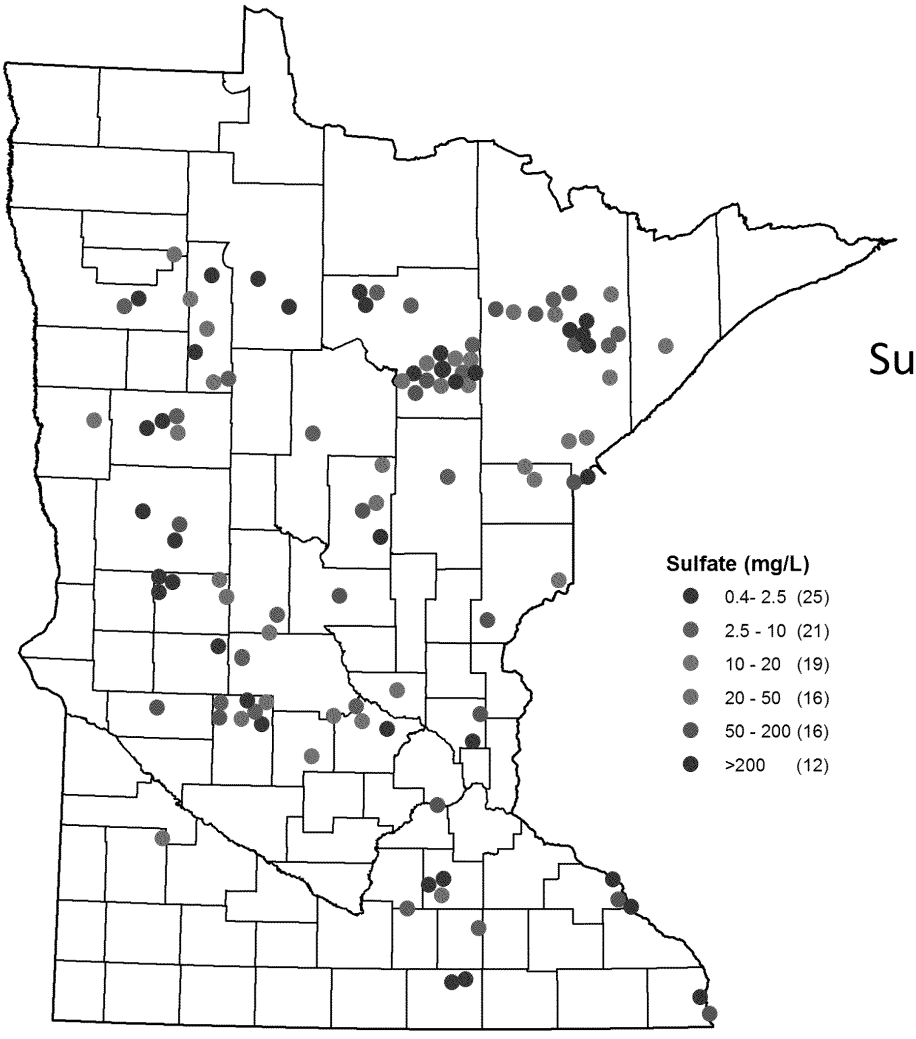
$$[SO_4^{2-}] = 0.002525 \times [Ca^{2+}]^{2.899} \times [Cl^{-}]^{-1.410} \times [Mg^{2+}]^{1.956}$$

Then, substitute 0.165 milligrams per liter for the sulfide concentration….producing the Calculated Protective Sulfate Concentration (CPSC):

$$CPSC = 0.000136 \times [Cl^{-}]^{-1.410} \times [Mg^{2+}]^{1.956}$$

Data from water bodies with wild rice where 3 or more sediment samples were taken within 1,000 feet of each other

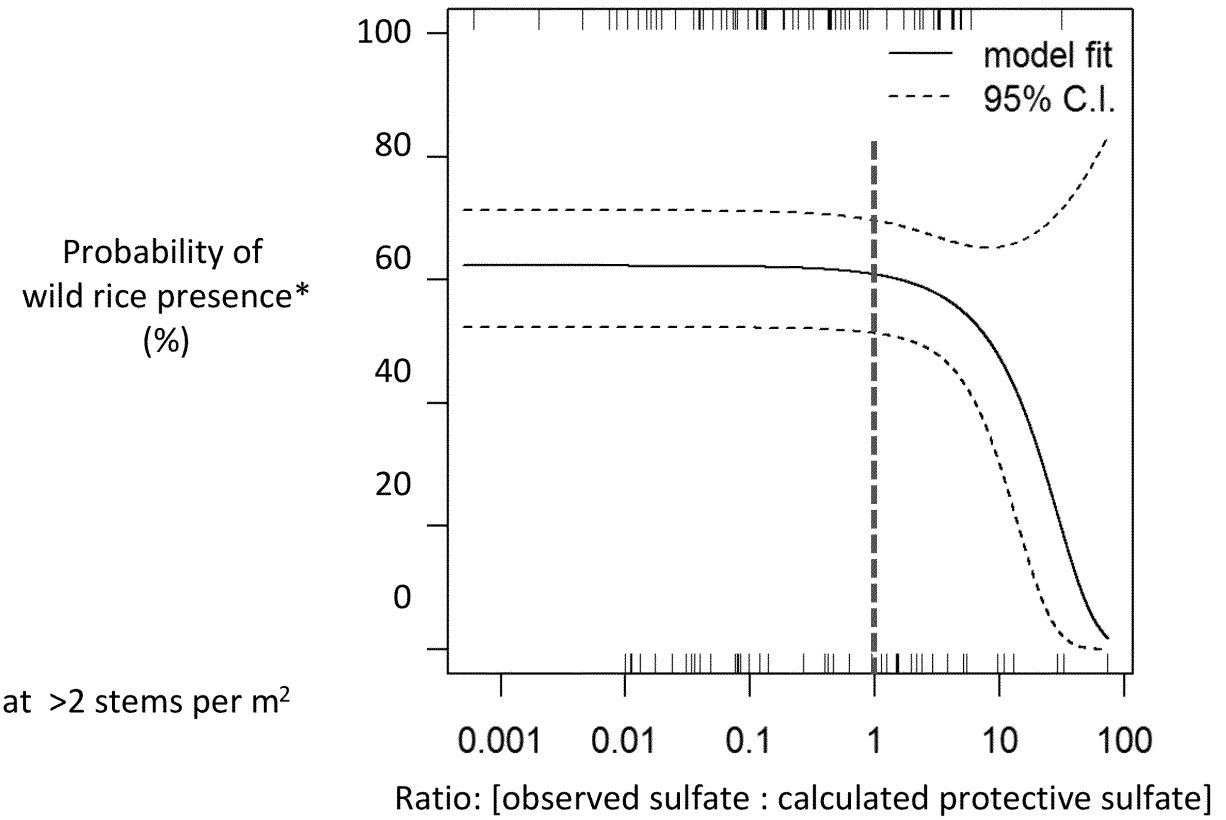




Sulfate concentrations that would produce porewater sulfide concentrations of 165 micrograms per liter

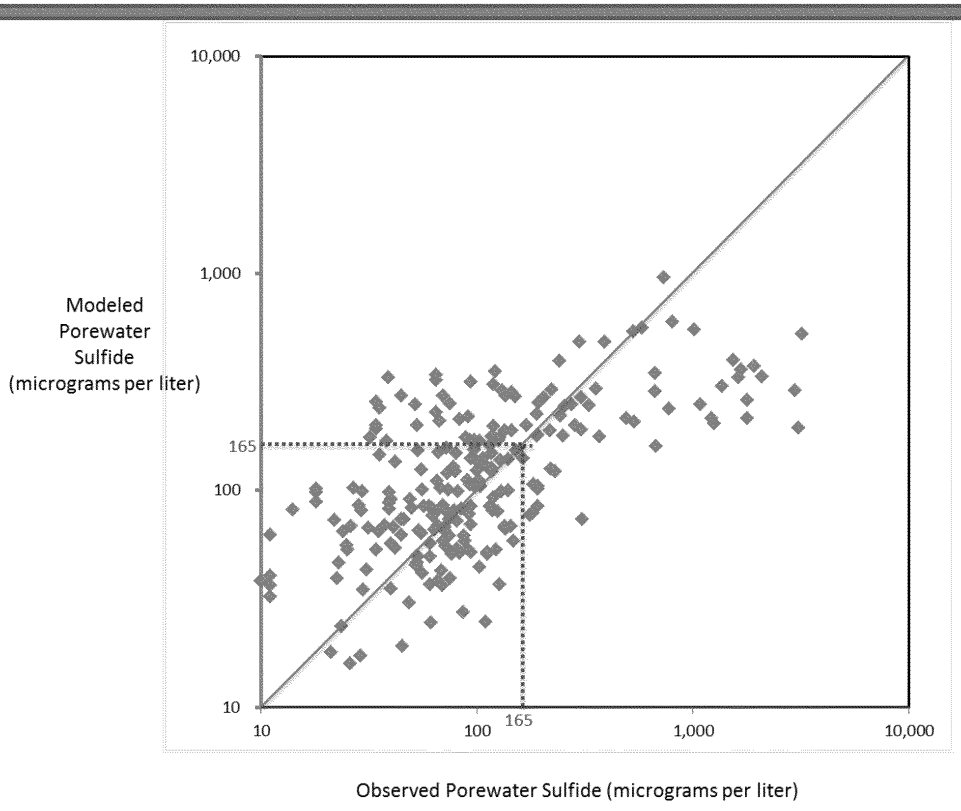
(averaged at sites where multiple sediment samples were taken)

Probability of Wild Rice Presence as a function of the ratio [observed sulfate]:[calculated protective sulfate]



*Present at >2 stems per m^2

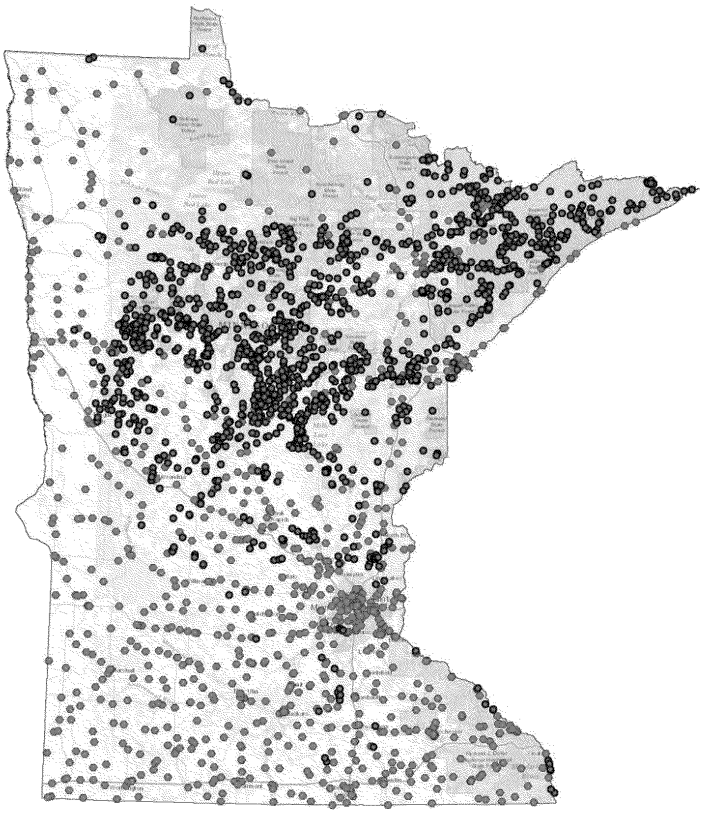
New Slide (July 7, 2015): Modeled porewater sulfide compared to observed



New Slide (July 7, 2015): MPCA activity since May 19, 2015

- Collect and analyze sediment samples from wild rice waters to determine number needed.
- Re-examine structural equation model:
  - Evaluate various subsets of data
  - Examine data for outliers
- Re-examine binary logistic regression
  - Evaluate subsets of data (similar to SEM)
  - Examine data for outliers
  - Examine effect of different stem density thresholds for definition of presence.

NPDES wastewater facilities and draft wild rice waters



Implementation Questions

- Sediment sampling protocol
- How to address variability in sampling results
- Monitoring priorities
- Translating results to permit limits – distance, duration…
- Data requirements for identification of additional wild rice waters
- Other?

Next Steps -- Approach

- Receive feedback on draft proposal
- Evaluate additional research
- Additional sampling to inform implementation questions
- Refine proposal as needed; develop technical support document
- Begin rulemaking process
  - Request for comments
  - Public meetings
  - Administration law judge hearing
  - Adopted in State Register
  - EPA review and approval

Thank You!

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